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Title:

**PROCESS FOR PREPARATION OF LATEX WITH AN ULTRAFINE PARTICLE SIZE**

## Summary

The present invention concerns a process for preparation of an aqueous dispersion containing between approximately 15 and 50 wt.% of solid products, which consist of the following steps:

a) incremental addition of one or more ethylenically unsaturated monomers capable of polymerizing in an aqueous environment to a reactor containing water and up to 6.3 parts per 100 parts of said monomer of 1 or more surfactants,

b) incremental addition of one or more polymerization initiators to the reactor and

c) polymerization of said ethylenically unsaturated monomer or monomers in such a way that the average particle size of said polymerized monomers is less than 100 nm.

The aqueous dispersions according to the invention have a broad range of practical uses, especially in compositions for coating, especially for paint.

## Description

The present invention concerns aqueous polymer dispersions of extremely fine size and in particular dispersions based on acrylic material having an average particle size smaller than 60 nm. More specifically the aqueous polymer dispersions of the present invention are produced by incremental addition of monomer solutions and an initiator to an aqueous solution containing at least one emulsifier which is maintained in a smaller quantity.

At the present time numerous latex emulsions exists.

However, the particle sizes of these latexes are generally large, e.g., 120 nm and more.

US patent 4 177 177 by Vanderhoff et al. reports various processes for preparing polymer emulsions which may be used to produce a latex. The latexes generally have a particle size greater than 100 nm.

US patent 4 228 047 by Pippin et al. concerns an aqueous coating composition consisting of a polymer of at least 95 wt.% vinyl acetate and at least 0.1 wt.% maleic anhydride which has

improved compatibility with a starch-based binder.

Japanese patent application JP-A 52103588 by Asahi Dow concerns a composition for carpet backing which contains 100 weight parts (in terms of solid products) of a copolymer latex: 200-350 parts by weight of an inorganic charge and a thickener consisting of 30-60 wt.% of

a) 20-70 wt.% butadiene

b) 5-30 wt.% styrene

c) 1-5 wt.% methyl methacrylate and

d) an ethylenic series of unsaturated carboxylic acid, and which has an average particle diameter of 60-120 nm.

By using the latex with small particle diameter to back carpets one avoids the formation of blisters.

Belgian patent BE-A 8 12 139 by DeSoto Inc. concerns opaque coatings obtained from a latex composed of an aqueous suspension of small and large resin particles, the large particles having a  $T_g$  lower than that of the small ones and having an average diameter which is more than double that of the small particles, the latter comprising 20-65 wt.% of the total particles. The particles are such that neither the large nor the small ones can combine when the latex is dried to form a noncellular film. The small particles yield a powder under such conditions. The small particles are preferably polystyrene and the large ones a vinyl acetate copolymer and the ester of an alcohol with 4-18 carbon atoms and an unsaturated carboxylic acid. The composition contains a minimal quantity of solvent and rapidly forms an

opaque coating of low porosity after drying. It may be used for lipstick, for crayons etc.

British patent GB-A 1 100 569 by the Dow Co. concerns acrylic polymer latexes containing large and small particles prepared

1) by heating water containing a soluble catalyst up to 85°C in an inert atmosphere

2) adding \_ of a mixture of monomers

3) conducting the polymerization during at least 15 minutes,

4) adding an aqueous solution of an anionic emulsifier and an aqueous solution of a polymerization catalyst and

5) adding the remaining monomer continuously over a period of at least 45 minutes.

US patent 3 711 435 by DuPont and Co., concerns a colloidal aqueous stable dispersion prepared by mixing

1) a copolymer of 20-80 wt.% ethylene and 80-20 wt.% amino-alkyl acrylate,

2) an acid having a dissociation constant of  $10^{-5}$ , and

3) water in a proportion which results in a solids content of 5-30 wt.% and a degree of neutralization of the amino groups of the polymer of at least 40%.

The mixing is performed at a suitable temperature for dispersing the polymer into the particles of a size smaller than 10 nm. The dispersions obtained have very small particles sizes sp that they may be applied in a fine layer on substrates of aluminum to produce coatings free of bubbles and may be used as

flocculants for separating a material in suspension from water. N,N-dimethylaminoethyl methacrylate is a suitable comonomer.

Japanese Patent Application JP-A 52-123478 by Kurraray concerns compositions prepared by emulsion polymerization of unsaturated monomers in the presence of a protective colloid which is prepared by splitting copolymers solubilized in water in the presence of free radicals and heating them. The composition contains maleimide and/or N-substituted maleimide units and  $\alpha$ -olefin units as essential constituents of the basic chain.

An article by Ugelstad El-Aasser and Vanderhoff, Journal of Polymer Science, Polymer Letter Edition, 11, p 503, 1973, concerns the preparation of latex particles by polymerization a mini-emulsion of a system of mixed emulfier including a surfactant and a cosurfactant of an alcohol or alkane with a long chain by exposure to ultrasound.

An article by Atik and Thomas, Journal of the American Chemical Society, 103, p. 4279, 1981, concerns aqueous micro-emulsions of polymers of styrene obtained by bulk polymerization, having an average particle size by number of approximately 20 to approximately 35 nm, by using a emulsifying mixture of cetyl trimethylammonium bromide and hexanol, then performing polymerization with an azobisisobutyronitrile soluble in oil and irradiating them. However, the content of solid products was very low, less than 2% and the quantity of emulsifier used was approximately 1.5 times the quantity of polymer by weight.

An article by Jayakrishnan and Shah, Journal of Polymer

Science, Polymer Letters, 22, p. 31: 1984, concerns bulk polymerization of particles in microemulsion of polystyrene or methyl methacrylate having an average numerical particle size of approximately 10-60 nm by using sodium dihexasulfosuccinate and the sequential copolymers of ethylene oxide-propylene oxide as emulsifying mixtures and an oil-soluble initiator such as benzoyl peroxide.

However, the weight ratio of the emulsifier to the monomer was approximately 1 to 1 and the microemulsion could not be diluted with water.

Canadian Patent application CA-A 2 013 318 by BF Goodrich concerns a process for production of aqueous polymer microemulsions with a very fine size. The process uses the incremental addition of a solution of monomer charge in an aqueous solution including one or more emulsifying agents and one or more water soluble or oxidoreduction [redox] initiators.

While this process may be used to prepare such microemulsions it is deficient in the extent that the emulsion has a tendency to become discolored and that it is extremely difficult to obtain emulsions having a profile of a narrow range of particle sizes.

An article by Okuba et al, "Preparation of assymetric, polymer film by emulsion blend technique, Colloid and Polymer Science, 268, pp. 1113-1117 (1990) describes the mixing of two emulsions of different particle sizes to determine the adhesive properties of such mixtures. One of the emulsions initially used

is an emulsion of poly(ethylacrylate-methylmethacrylate) having a particle size of 0.02  $\mu\text{m}$ . According to the article this emulsion is prepared by combining the monomers in a glass vial with water, sodium sulfite, potassium persulfate and sodium dodecyl sulfate. The order of the process of addition of the different reagents, initiators and emulsifiers is not specified.

European Patent Application EP-A 0 429 207 by Rohm & Haas concerns a process for coating a substrate with the an aqueous composition. The coating composition is an aqueous dispersion of particles of copolymer having mutually incompatible phases and having an average particle size of approximately 20-70 nm. The dispersion is prepared by the techniques of emulsion polymerization. In the preferred modes of realization the particles have a core-shell morphology where the core has a  $T_g$  of at least 45°C and the shell at  $T_g$  lower than 35°C.

Despite the limitation above there still exists a need for a process in this technique for the preparation of a latex in emulsion with an ultrafine size which does not become discolored, has a narrow particle size distribution, is easily reproducible and which uses a minimal quantity of surfactant.

According to the present invention a process has now been found for preparing a latex in emulsion with ultrafine particle size which does not become decolored, has a narrow particle size distribution, is easily reproduced and uses a minimal quantity of surfactant. The process is specifically characterized by the incremental introduction of monomers and initiators into an

aqueous reaction medium so that the ionicity of the reaction medium remains constant.

One mode of realization of the invention consists of a process for producing a dispersion based on water containing between 15 and 50 wt.% of solid products, which consists of the following steps:

a) incremental addition of one or more ethylenically unsaturated monomers capable of polymerizing in an aqueous environment to a reactor containing water and up to 6.3 parts per 100 parts of said monomer of one or more surfactants,

b) incremental addition of one or more polymerization initiators to the reactor and

c) polymerization of said ethylenically unsaturated monomer or monomers in such a way that the average particle size of said polymerized monomers is less than 100 nm.

In this preferred mode of realization the process uses monomers derived from acrylic acids and esters and yields a latex with an ultrafine size and an average particle size less than 50 nm.

Another mode of realization of the present invention consists of an aqueous dispersion capable of being prepared by the process above. The polymer latex of ultrafine particle size is resistant to coagulation and may be diluted with water. The particles of the polymer have several physical characteristics such as good film formation, good penetration into porous substrates, a specific surface-to-volume ratio that is very high, a



monomodality and the like.

The new dispersions may be used in the fabrication of products for preservation of wood, as polymer and metal coatings, adhesives, chemical products for waterproofing, sizes for textiles and agrochemical products, pharmaceutical products, chemical products for the petroleum sector, inks, for papermaking, as rheology modifiers, cosmetic products, ultraviolet light diffusion agents, and in biomedical and immunoassay applications.

One purpose of the present invention is to produce a latex emulsion with ultrafine particle size which does not become discolored, has a narrow granulometry, is easily prepared and which uses a minimal quantity of surfactant.

An additional objective of the present invention to devise an ultrafine latex emulsion which is resistant to coagulation, is a good film former, penetrates well into porous substrates, has a specific surface-to-volume ratio that is very high and has monomodality.

These objectives as well as others become obvious to specialists in the field from the detailed description of a preferred mode of realization.

In the following description a certain terminology was used for purposes of clarity. Such terminology is intended to allow for the mode of realization described as well as the equivalent techniques which function in a similar manner for a similar purpose in order to obtain a similar result. The ultrafine latexes are prepared by incrementally adding one or more ethylen-

ically unsaturated monomers capable of polymerizing in an aqueous medium and incrementally adding a polymerization initiator to a reactor containing water and one or more surfactants, then allowing the polymerization of the ethylenically unsaturated monomers to take place in such a way that the average size of the particles of said polymerized monomers are smaller than 100 nm. The term "incremental addition" defines a form of addition of a small quantity of monomer and/or initiator of the total to an aqueous solution over a long period of time until the total amount of the monomer solutions and initiator have been added. This includes cyclic additions, interrupted additions, combinations of the latter, and the like. Preferably the addition of the monomer and the initiator is continuous and has a constant rate over a period of time.

One may choose any ethylenically unsaturated monomer that is capable of polymerizing in an aqueous medium as the initial material. An especially preferred monomer is one or any of the following monomers: (meth)acrylic acids and esters, acrylonitrile, styrene, divinyl benzene, vinyl acetate, ethylenically unsaturated carboxylic acids, acrylamide, methacrylamide, vinylidene chloride, butadiene and vinyl chloride. The solid products of the dispersion which are produced may assume the form of homopolymers (i.e. only one type of monomer chosen) or copolymers (i.e. one selects mixtures of two types of monomers or more, this includes specifically the terpolymers and the polymers derived from 4 monomers or more).

The use of acrylic acids and esters is most preferred. The acrylic polymers of the present invention are obtained from one or more acrylate monomers corresponding to the formula:



where  $\text{R}_1$  is preferably a hydrogen or an alkyl group having 1 to 4 carbon atoms and  $\text{R}_2$  is an aliphatic group having 1-20 carbon atoms. In the most preferred modes of realization  $\text{R}_1$  represents a methyl group and  $\text{R}_2$  is an alkyl group having 1-20 carbon atoms.

The monomers specifically used within the scope of formula (I) include methyl methacrylate, ethyl acrylate, butyl acrylate, methacrylic acid, acrylic acid and mixtures of the latter.

Other monomers or initial compounds which may be used to produce the ultrafine latexes are well known to the art. Examples are given in The Encyclopedia of Chemical Technology, Kirk-Othmer, John Wiley & Sons, vol. 14, pp. 82-97 (1981). To the degree necessary this passage is incorporated here as a reference.

During the preparation of the copolymers which are a batch obtained from acrylic monomers, the quantity of acrylic monomers is typically approximately 30-99% of the total quantity of monomer, the quantities ranging from approximately 50 to 90% being preferred and the quantities ranging from approximately 60 to 80% being most preferred.

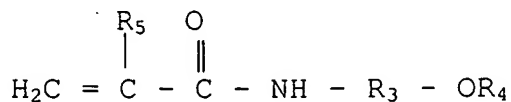
In addition, in the case of copolymerization with an acid such as methacrylic acid, the copolymer may include up to 60 wt. %

of the acid. This is much higher than the systems of prior art and permit the latexes to be used specifically in textile applications as the materials obtained are more easily dissolved in a base.

Moreover, during the preparation of the copolymer dispersions the separate monomers may be introduced into the aqueous reaction medium from the same feed container or from different feed containers.

For several applications, although this is not necessary, it may be desirable for the polymer produced to be crosslinked. This is accomplished by adding one or more crosslinking agents to the reaction medium.

Examples of crosslinking agents include the monofunctional compounds such as N-alkylol amines of the formula



where R<sub>3</sub> is an alkyl group having from 1 to 10 carbon atoms, preferably 1 to 4 carbon atoms; R<sub>4</sub> is hydrogen or an alkyl group having 1-10 carbon atoms, preferably 1-4 carbon atoms, and R<sub>6</sub> is hydrogen or an alkyl group having 1 to 4 carbon atoms.

Specific examples of suitable crosslinking agents include N-methylol acrylamide, N-ethanol acrylamide, N-propanol acrylamide, N-methylol maleimide, N-ethylol maleimide, N-methylolmaleamic acid, the esters of N-methylolmaleamic acid, the N-alkylol amides, the vinyl aromatics such as N-methylol-p-vinylbenzamide and the like.

Another cross-linking agent which may be used is N-(isobutoxymethyl)acrylamide.

One may also use various compounds or difunctional monomers as effective crosslinking agents. They include compounds containing two olefinic groups such as divinylbenzene, divinyl-naphthalene, divinylcyclohexane and the like; various diacrylate and dimethacrylate esters or aliphatic diols in which the ester fraction has from 1 to 10 carbon atoms, and preferably an alkyl group when the diol fraction has 2-8 carbon atoms.

Examples of these materials include ethylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate and butylene glycol.

Other crosslinking agents are described in the Journal of Applied Polymer Science, Vol 34, pp. 2389-2397 (1987), John Wiley & Sons in an article titled "New cross-linking agents for vinyl polymers". To the degree necessary this article is here incorporated as a reference.

The quantity of crosslinking agents, if one is used, is generally approximately 0.05 to 10 wt.%, preferably 0.1 to 5 wt.% and again most preferably approximately 0.1 to 1.0 wt.% relative to the total weight of all monomers added.

One also adds incrementally to the aqueous reaction medium one or more polymerization initiators, preferably a thermal free-radical initiator.

The polymerization initiator may take the form of numerous well-known initiators such as the azo, peroxide, persulfate and

per-ester initiators and may be water soluble or soluble in the monomer. The quantity of initiator added to the solution typically ranges from 0.05 to 2 wt.% of the emulsion, the quantities ranging from 0.1 to 1.0 wt.% being especially preferred and quantities ranging from 0.1 to 0.5 wt.% being most preferred. The radical initiator added is preferably an initiator of the azo-type (azo bis nitrile) (water or oil soluble) such as 2,2-azo-bis-isobutyronitrile, 2,2-azo-bis-3-methylpropane nitrile), 2,2'-azo bis-(2,4-dimethylpentane nitrile), 2,2'-azobis-(2-methylbutane nitrile), 1,1'-azobis (cyclohexane carbonitrile), 2,2'-azo-bis-2,4-dimethyl-4-methoxyvaleronitrile), 2,2'-azo-bis-(2,4-dimethylvaleronitrile) and 2,2'-azobis-(2-amidinopropane)hydrochloride.

Other free radical initiators which may be chosen include the peroxide materials such as benzoylperoxide, cumene hydroperoxide, hydrogen peroxide, acetyl peroxide, lauroyl peroxide, persulfate materials such as ammonium persulfate and peresters such as t-butylperoxypivalate,  $\alpha$ -cumyl peroxypivalate and t-butyl peroctoate.

Examples of commercially available initiators which may be chosen include WAKO (V-50), Vazo 52, Bazo 64, Vazo 67 and Lubersol 112. These commercial initiators may be included with the monomer charge.

In the case of water-soluble initiators such as the peroxides and persulfates it is critical that during the polymerization the ionicity of the reaction medium be held constant. This

is accomplished by feeding part of the water of the aqueous reaction medium and adding this water separately to the flow of the initiator charge. The need to maintain a constant ionicity is observed when one obtains a subsequent conventional treatment for the residual monomer with ammonium persulfate and sodium metabisulfite. It is formed from large quantities of coagulum which reduces the efficiency of the process. Similarly, a charge of conventional initiator composed of ammonium persulfate and representing 1-3 wt.% of the total volume of water causes the agglomeration of the polymer particles during the entire addition of the initiator.

It has been found that by maintaining a constant ionicity in the reaction mixture the agglomeration may be avoided thus obtaining an emulsion with a more uniform particle size. By diluting the water-soluble initiator with the appropriate quantity of water the ionic resistance of the initiator system is the same as that of the content of the reactor at any moment during the reaction/introduction of initiator. It is supposed that this apparent ionicity (expressed in the number of charges per volume) permits the migration by controlled diffusion of the charged species such as ammonium persulfate and the ionic surfactants from the drops to the reaction mixture and vice-versa.

The use of a highly concentrated initiator solutions would permit greater variation of the ionic concentration of the air immediately surrounding a drop of initiator. The hypothesis is that the massive variation of the charge density overrides the

stabilizing forces exercised by the residues of surfactant and initiator.

One can obtain the same ionic equilibrium by the suitable choice of an initiator soluble in the monomer, of neutral charge such as an initiator of the azo type sold as Vazo 52 (2,2'-azobis-2,4-dimethylvaleronitrile) or VAZO 64 (2,2'-azobisisobutyronitrile). In these cases the entire quantity of initiator is contained in the monomer charge.

It is believed that the concept of maintaining a constant ionicity in the reaction medium has not been utilized to form ultrafine polymer latexes of uniform size until the present invention. Prior art in the field of ultrafine latexes describes that the initiator is contained in the aqueous reagent or added "all at once".

According to the process of the present invention the monomer(s) and initiator(s) are introduced into an aqueous reaction medium which contains water and at least one or more emulsifiers. The emulsifiers are generally surfactants and may therefore be cationic, non-ionic, anionic, amphoteric or similar copolymerizable surfactants, the anionic surfactants being generally desired. Generally the type of emulsifiers used are those which may be used in polymerizations of conventional latexes. As the specialist in the field will recognize, one criterion for the choice of a surfactant is its compatibility with the initiator.

Examples of amphoteric surfactants which are suitable



include the salts of an alkali metal, alkaline earth metal, ammonium or ammonium-substituted alkyl amphocarboxyglycinates and alkyl amphocarboxypropionates, alkyl amphopropionates, alkyl-amphodiacetates, alkyl amphoglycinates and alkyl amphopropionates where alkyl represents an alkyl group having 6 to 20 carbon atoms. Other amphoteric surfactants include the alkyl iminopropionates, alkyl iminodipropionates, alkyl amphopropylsulfonates having between 12 and 18 carbon atoms, the alkyl betaines and amidopropylbetaines and the alkyl sultaines and alkylamidopropyl hydroxysultaines where alkyl represents an alkyl grouping having 6 to 20 carbon atoms.

The anionic surfactants which may be chosen include any of the known hydrophobic surfactants attached to a solubilizing carboxylate, sulfonate, sulfate or phosphate group including their salts. The salts may be the salts of sodium, potassium, calcium, magnesium, barium, ion, ammonium, and the amine of such surfactants.

Examples of these anionic surfactants include the water soluble salts of the alkylbenzene sulfonates having between 8 and 22 carbon atoms in the alkyl groups, the alkyl ether sulfates having between 8 and 22 carbon atoms in the alkyl groups, the salts of an alkaline metal, ammonium and alkanolammonium or the organic products of the sulfuric reaction having in their molecular structure an alkyl group or alkaryl group containing 8-22 carbon atoms and a sulfonic or sulfuric acid ester group. One prefers the linear sodium and potassium alkyl sulfates. In

particular it is preferred to use sodium lauryl sulfate (sodium dodecyl sulfate). Another type of anionic surfactant that is preferred are the alkylbenzene sulfonates in which the alkyl groups contains between 9 and approximately 15 and preferably between approximately 11 and 13 carbon atoms in a linear or branched chain configuration and even more preferably a linear straight chain having a central alkyl group of approximately 11 carbon atoms.

In certain modes of realization one may use mixtures of anionic surfactants, mixtures of alkyl or alkylaryl sulfate or sulfonate surfactants where alkylaryl is especially preferred. Such modes of realization include a mixture of alkaline metal salts, preferably sodium salts, of alkylbenzene sulfonates having approximately 9-15 and preferably between 11 and 13 carbon atoms, with the salt of an alkali metal, preferably sodium, an alkyl sulfate or alkyl ethoxysulfate having 10 to 20 and preferably 12 to 18 carbon atoms and an average degree of ethoxylation of 2-4.

Specific anionic surfactants which may be chosen include the linear alkyl benzene sulfonates such as dodecyl benzene sulfonate, decylbenzene sulfonate, undecylbenzene sulfonate, tridecyl benzene sulfonates, nonylbenzene sulfonate and the sodium, potassium, ammonium and triethanolammonium and isopropylammonium salts of the latter.

Examples of nonionic surfactants used include the condensates of ethylene oxide with a hydrophobic fraction which has a hydrophil-lipophil equilibrium (HLB) of average degree between

approximately 8 and 16 and preferably between 10 and approximately 12.5.

These surfactants include the condensation products of the primary or secondary aliphatic alcohols having approximately 8 to 24 carbon atoms in a linear or branched configuration with approximately 2 to 40 and preferably 2 and 9 moles of ethylene oxide per mole of alcohol. Other appropriate nonionic surfactants includes the condensation products of alkylphenols of approximately 6 to 12 carbon atoms with approximately 3 to 30 and preferably between 5 and 14 moles of ethylene oxide.

Examples of such surfactants are sold under the tradenames of Igepol CO 530, Igepol CO 630, Igepol CO 720 and Igepol CO 730 by Rhone-Poulenc.

Still other suitable nonionic surfactants are described in the US patent 3 976 586. To the extent necessary this patent is expressly incorporated here as a reference. Examples of cationic surfactants include cetyl trimethylammonium bromide. Other surfactants which may be used include those described in McCutcheons "Detergents and emulsifiers" 1978, North American Edition, Edited by the McCutcheon Division, MC Publishing corp., Glen Rock New Jersey, as well as in various subsequent editions. To the degree necessary this publication is incorporated expressly here as a reference.

In practice the quantity of surfactant present in the aqueous phase ranges from approximately 0.5 to 6.3 wt.% of the monomer added. The quantities between 0.5 and approximately 3.0

wt.% of total added monomers are most preferred and the quantities between 1.0 and approximately 3.0 wt.% of total monomers added are more preferred. In general the particle size of the latex decreases with the increasing quantities of added surfactant to approximately 3.0 wt.%. Beyond 3.0 wt.% of surfactant the decrease in particle size is much less pronounced.

The reaction medium may include between approximately 0.5 and 10.0 wt.% of added monomers and other optional additives to furnish the specific functional properties of the final latex. Examples of such additives include plasticizers such as polyethylene glycol, antifoam agents, pigments, coloring agents and dyes, antibacterial agents, perfumes, pharmaceutical products, enzymes and other biologically active agents, agrochemical products, ultraviolet activated agents, stabilizers and rheology modifiers.

To produce the new latex of the present invention one uses a process of semicontinuous or continuous polymerization. This includes the addition of the monomer, introduction of the cross-linking agent if necessary and the initiator solutions incrementally into the reactor which is typically brought to temperatures of approximately 45 to 90°C and includes water and one or more emulsifiers over a period of time, as opposed to discontinuous addition. Optionally the reactor may contain a small quantity of monomer before the beginning of the incremental polymerization which acts as a "seed". A small quantity of monomer is generally less than 30 wt.% and preferably no greater than approximately 10

wt.% of the total monomer used. The rate of addition of the monomer is generally regulated by various factors such as the size of the reactor, the increase in temperature of the exothermic reactions, the cooling capacity of the reactor and the like such that the reaction temperature is generally maintained at a value of in a specific range.

The quantity of the emulsifier or emulsifiers contained in the reactor is generally at least 50 or 60 wt.%, preferably at least 70 wt.%, more preferably at least 80 wt.% and most preferably at least 90 wt.% of the total quantity of emulsifiers. The remaining emulsifier, if there is any, is introduced with the flux of the charge of monomer or initiator.

The reactor may be held at lower temperatures than the ambient temperature (10-20°C) up to the boiling point of the aqueous solution. The pressure of the reaction is generally atmospheric but it may be raised if necessary to aid in the polymerization.

As described above the charge of monomer and the charge of initiator may be the same charge if the initiator is soluble in the monomer. In addition if the initiator is water soluble and charged as ammonium persulfate, it is introduced in such a way that the ionicity in the total reactor contents is maintained at a constant level. This is typically accomplished by initially transferring a quantity of water from the reactor into the initiator charge to create ionic concentrations which are essentially equal both in the feed container and in the reactor.

The introduction of the initiator solution on an incremental base causes a concentration of free radicals generally in a permanent mode during the entire addition of the monomer. This permanent free radical concentration avoids low concentrations of radicals observed with charges containing the initiator alone and during prolonged feeding times. It is this continuous and easy availability of free radicals which permits the formation of new chains and particles which effectively compete with the addition of monomer to the existing particles. Relative to systems of initiation by introduction all at once according to prior art the process of the invention clearly improves the monodisperse character of the latex obtained. The polymerization continues until all of the monomer(s) and initiator have been added to the reactor and until almost all of the monomer charge has been converted into a polymerized form. The polymerization is generally continued until one obtains a high conversion such as greater than 80%, preferably at least 90-95% and most preferably at least 98% for a complete conversion.

Independently of the specific type of monomer chosen for the polymerization the process described above the average size of the polymer particles is very small. The term "particle size" refers to the median size of the average particles by volume measured by spectroscopy by photocalibration. The polymer latex is produced according to the present invention has an average particle size in volume that is very small, 100 nm or less, the preferred average particle sizes ranging from approximately 1 to

approximately 60 nm, more preferably between 5 and 40 nm, even more preferably 10 and 30 nm and ideally between approximately 10 and 20 nm. Generally one may obtain any range of particle size above as a function of the specific desired final properties.

In addition, and in particular, because of the system of incremental introduction of the initiator used, the spectrum of particle sizes produced is limited. In practice, the typical deviation for each latex of the desired size is no greater than 4 nm.

The process above yields a polymer latex which is stable with respect to coagulation to the extent that it can be diluted with water without the appearance of coagulation. The content of solid products in latex is relatively high, approximately 5 to 55 wt.%, desirably approximately 15% to 50% by weight and more preferably approximately 20 to 40 wt.% and most preferably approximately 25 to 35 wt.% based on the total weight of the aqueous polymer latex. The properties of the polymer latex depend essentially on the monomer chosen for polymerization. For example, the one glass transition point of the polymers may range from approximately  $-54^{\circ}\text{C}$  to more than  $130^{\circ}\text{C}$ .

The polymer latexes of the present invention because of their extremely fine size are used in numerous applications such as good preservatives, polymer and metal coatings, adhesives, chemical products for water proofing, textile sizes, agrochemical products, pharmaceutical products, chemical products for the petroleum field, inks, paper products, rheology modifiers,

cosmetic products, personal care products, ultraviolet light diffusion agents, solar screens and biomedical and immunoassay applications. Although they are latexes at the structural level they frequently come close to the properties of the solution type. Moreover they may be used alone or in combination with other materials such as emulsions of a greater particle size in order to yield products having specific utilizations.

The invention can be better understood by referring to the following examples:

#### **Example 1**

An aqueous polymer latex of methyl methacrylate is prepared as follows: 100 parts per hundred (ppc) of methyl methacrylate are mixed with 0.5 ppc of Vazo 52, a thermal initiator (2,2'-azobis-(2,4-dimethylvaleronitrile) which is soluble in methyl methacrylate. This monomer/initiator solution is introduced uniformly over 3 hours into a 1 liter glass reactor containing 185 ppc of water and 3 ppc of sodium dodecylsulfate. The reactor is held at 85°C and constantly stirred. At the end of the monomer addition the reactor is held at 85°C for 1 hour longer. The reaction mixture is then brought to an almost total conversion by treatment with 0.015 ppc of t-butyl hydroperoxide and 0.015 ppc of sodium metabisulfite at a temperature of 62°C: This synthesis terminates in an aqueous polymer latex containing 35 wt.% of solid products. The average particle size measured by a Niacomp 370A is 14 nm. This polymer latex is translucent because of the small size of the latex particles. The latex is



blue in color and has a Tg of approximately 105°C.

#### **Example 2**

An aqueous polymer latex of butyl acrylate, methyl methacrylate and methacrylic acid is prepared by the same process as in example 1. The composition of the monomer/initiator solution is 65 ppc butyl acrylate, 25 ppc methacrylic acid, 10 ppc methyl methacrylate and 1 ppc VAZO 64 (2,2'-azo-bisisobutyronitrile). This process yields a latex with a total solids content of 25 wt.% and an average particle size measured in volume of 14 nm. The latex is transparent, blue in color and has a Tg of approximately -5°C.

#### **Example 3**

An aqueous polymer latex of styrene, butyl acrylate, and methacrylic acid is prepared as follows: 65 ppc of butyl acrylate, 25 ppc of methacrylic acid and 10 ppc of styrene are carefully mixed together to form a charge solution. In a separate feed container one adds 0.25 ppc of ammonium peroxydisulfate to 65 ppc of water. In a separate reactor one adds 3 ppc of sodium dodecyl sulfate to 244 ppc of water and heats to 85°C with constant stirring. The reason for preparation of separate solution of aqueous initiator is to permit a constant ionicity in the reactor during the operating procedure of synthesis. 10% of the total volume of the solution of ammonium peroxydisulfate is added to the heated mixture and the solutions of initiator and monomer begin to be introduced at a flow rate which permits a regular introduction of charge solutions over an interval of

3 hours. The reaction mixture is stirred for 30 minutes longer and then cooled to 62°C. 0.10 ppc of sodium metabisulfite is dissolved in 24 ppc of water and introduced into the reaction mixture over an interval of 1 hour. The reaction temperature is then held at 85°C for 1 hour. The mixture is then cooled to ambient temperature and filtered. This charge results in an aqueous polymer latex containing 23.3 wt.% of solid products. The average particle size by volume measured by photocalorrelation spectroscopy is 34 nm. The latex is transparent and blue in color and has a Tg of approximately -5°C.

#### **Example 4**

0.25 ppc of ammonium persulfate dissolved 0.52 ppc of water are added to a solution containing 4.17 ppc of sodium lauryl sulfate and 313 ppc water. After a startup period of 5 minutes a mixture of 53 ppc of butyl acrylate and 47 ppc of methyl methacrylate is introduced into the solution over an interval of 2 hours. The temperature is then held at 92°C for half an hour and the mixture is then cooled and filtered. One obtains a blue-gray latex having a solids content of 24.85%. This latex has an average particle size smaller than 30 nm and a Tg of -5°C.

#### **Example 5**

0.15 ppc of ammonium persulfate dissolved 0.3 ppc of water is added to a solution containing 2.57 ppc of sodium lauryl sulfate and 241 ppc water. After a startup period of 5 minutes a mixture of 43 ppc of butyl acrylate and 57 ppc of methyl meth-

acrylate is introduced into the solution over an interval of 2 hours. The temperature is then held at 92°C for half an hour and the mixture is then cooled and filtered. One obtains a blue-gray latex having a solids content of 23.10%. This latex has an average particle size smaller than 30 nm and a Tg of 0°C.

#### **Example 6**

Two separate charges, one part consisting 0.32 ppc of ammonium persulfate dissolved 85 ppc of water, the other charge composed of 10 ppc styrene, 25 ppc methacrylic acid, and 65 ppc butyl acrylate, are added continuously and simultaneously to a solution containing 3.1 ppc of sodium lauryl sulfate and 245 ppc water heated at 25°C. Each separate charge is introduced over a period of 2.5 hours in such a way that the two flows of charge are exhausted at the end of approximately 2-5 hours. A solution containing 0.1 ppc of sodium metabisulfite dissolved in 24 ppc water is then introduced into the reaction mixture over half an hour. The temperature is maintained for an hour and the reaction mixture is then cooled to ambient temperature and filtered. One obtains a blue transparent latex having a solids content of 23.3% and an average particle size of approximately 14 nm.

#### **QUANTITATIVE AND QUALITATIVE ESSAY**

##### Wood penetration properties

A test was performed to determine the penetration capacity of wood by the latex of the invention relative to the commercially available products. The following operating mode

was used for the tests:

1. Solutions of 10% solids of each latex are prepared by diluting each latex with a suitable quantity of distilled water.
2. A pine dowel is cut into 3 inch pegs, and each peg is immersed in each latex solution for 3 hours.
3. Each peg is dried under ambient conditions for 1 night.
4. A colored solution of 2% nigrosine is prepared and each peg is immersed dry in the solution for 24 hours.
5. Each peg is removed and dried under ambient conditions for 1 night.
6. Several transverse cuts are made in each peg and evaluated in terms of dye penetration. The latex samples tested are:

Sample A: Latex of example 4

Sample B: Latex of example 5

Sample C: Joncryl 537, 46% solids (S. C. Johnson)

Sample D: Reichhold 40-423, 46% solids (Reichhold Chemical)

Sample E: UCAR 429, 47% solids (Union Carbide)

The particle size and the relative penetration of the dye for each sample are presented in Table 1.

**Table 1**

Sample	Particle size	Penetration
A	< 30 nm	minimal
B	< 30 nm	minimal
C	90 nm	slight
D	100 nm	appreciable
E	150 nm	significant

The minimal penetration found in the case when the materials of the invention were used shows that the latexes of very small particle size penetrate wood better than conventional latexes. Consequently, the material of the invention form significantly better protective coatings for wood than commercial materials.

#### Surfactant properties

The surface tensions of solutions of 10% of the solids of samples A, C, D, and E were analyzed by using a SensaDyne bubble surface tensiometer. The results are presented in Table 2. The surface tension is measured in dynes/cm.

Table 2

Sample	Particle size	Surface tension
A	< 30 nm	57.3
B	< 90 nm	40.8
D	100 nm	57.2
E	150 nm	47.9

The penetration capacity depends largely on the wetting capacity. If a product does not wet a surface well, there is little chance of penetrating said surface. The higher surface tension of sample A, a sample according to the invention, causes a net disadvantage for this product in the penetration studies.

However, the previous example shows that sample A has much better penetration of wood than the commercial samples (C, D, and E).

Hence the hypothesis that the particle size is much more significant than the surface at the level of determining the penetrating capacity of a latex. In addition the tests above were performed with 10% solutions of solid products. It is assumed that by using samples in a "clean" form, samples A and B would display even better results.

#### Textile sizing properties.

The latex of example 6 was compared with the commercial products Permaloid 150 and Permaloid 172, both made by Rhone-Poulenc for use as textile sizes. All of the samples were evaluated at concentrations of 7% and applied to the fibers and filaments of polyester with a laboratory sizing machine. The

abrasion resistance of the latex of sample 6 is approximately equal to that of Permaloid 150 and Permaloid 172. The advantage obtained by using the latex of the invention is the absence of neutralization before application. The conventional sizes such as Permaloid 150 and Permaloid 172 are applied in the form of polymer solution prepared by solubilizing with an alkali of a conventional polymer latex. The textile sizes based on the ultrafine latex of the invention are applied directly to the fiber without neutralization. This eliminates the need for an alkali and for monitoring the evolution of ammonia which is normally associated with the sizing of fibers and filaments and therefore confers significant advantages with respect to the commercially available materials.

The invention having been described in detail and with reference to preferred modes of realization, it has been shown that modifications and variations are possible without departing the scope of the attached claims.

#### **Claims**

1. Process for preparation of an aqueous dispersion containing between approximately 15 and 50 wt.% of solid products, characterized by the fact that it consists of the following steps:

a) incremental addition of one or more ethylenically unsaturated monomers capable of polymerizing in an aqueous environment to a reactor containing water and up to 6.3 parts per 100 parts of said monomer of 1 or more surfactants,

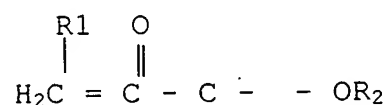
b) incremental addition of one or more polymerization initiators to the reactor and

c) polymerization of said ethylenically unsaturated monomer or monomers in such a way that the average particle size of said polymerized monomers is less than 100 nm.

2. Process as in claim 1 characterized by the fact that steps (a) and (b) are performed simultaneously.

3. Process as in claim 1 characterized by the fact that the ethylenically unsaturated monomer or monomers are chosen from the group consisting of (meth)acrylic acids and esters, acrylonitrile, styrene, divinyl benzene, vinyl acetate, ethylenically unsaturated carboxylic acids, butadiene, acrylamide, methacrylamide, vinylidene chloride, vinyl chloride and their mixtures.

4. Process as in claim 3 characterized by the fact that the ethylenically unsaturated monomer or monomers correspond to the formula



where  $\text{R}_1$  is a hydrogen or an alkyl group having 1 to 4 carbon atoms, and  $\text{R}_2$  is an aliphatic group having 1-20 carbon atoms.

5. Process as in claim 4 characterized by the fact that the ethylenically unsaturated monomer or monomers are chosen from the group composed of methyl methacrylate, ethyl acrylate, butyl acrylate, methacrylic acid, acrylic acid and mixtures of the latter.

6. Process as in claim 3 characterized by the fact that the



surfactant or surfactants are chosen from the group composed of anionic, non-ionic, cationic, amphoteric and copolymerizable surfactants.

7. Process as in claim 6 characterized by the fact that said surfactants contain one or more anionic surfactants present in a quantity of approximately 0.5-3.0 wt.% of the total quantity of monomer added.

8. Process as in claim 7 characterized by the fact that said anionic surfactant is chosen from the group composed of the water-soluble salts of the alkylbenzene sulfonates having between 8 and 22 carbon atoms in the alkyl group, the alkyl ether sulfates having 8 to 22 carbon atoms in the alkyl group and the salts of alkali metals, ammonium and alkanolammonium or the organic products of the sulfuric reaction having in their molecular structure an alkyl or alkaryl group containing 8 to 22 carbon atoms and a sulfonic or sulfuric acid ester group or their mixtures.

9. Process as in claim 8 characterized by the fact that said anionic surfactant is chosen from the group composed of linear alkyl sulfates and alkylbenzene sulfonates of sodium and potassium in which the alkyl groups contain between approximately 9 and 15 carbon atoms and mixtures of these.

10. Process as in claim 9 characterized by the fact that said anionic surfactant is sodium lauryl sulfate.

11. Process as in claim 3 characterized by the fact that said polymerization initiator contains a water-soluble initiator or an

initiator soluble in organic substances which is introduced in a quantity ranging from approximately 0.1 to 3 wt.% of said ethylenically unsaturated monomer(s).

12. Process as in claim 11 characterized by the fact that said polymerization initiator is soluble in said ethylenically unsaturated monomer or monomers and is chosen from the group consisting of azo-, peroxide, per-ester and oxido-reduction initiators.

13. Process as in claim 12 characterized by the fact that said polymerization initiator is chosen from the group composed of 2,2'-azo bis isobutyronitrile, 2,2'-azobis-3-methylpropane nitrile), 2,2'-azo bis-(2,4-dimethylpentane nitrile), 2,2'-azobis-(2-methylbutane nitrile), 1,1'-azobis(cyclohexane carbonitrile), 2,2'-azobis-2,4-dimethyl-4-methoxyvaleronitrile), 2,2'-azobis-(2,4-dimethylvaleronitrile) and 2,2'-azobis-(2-amidinopropane) hydrochloride.

14. Process as in claim 12 characterized by the fact that said polymerization initiator is introduced from the same container as the ethylenically unsaturated monomer(s).

15. Process as in claim 11 characterized by the fact that said polymerization initiator is water soluble and is added to the reactor in such a way that the reactor maintains the same ionicity for the duration of the polymerization reaction.

16. Process as in claim 15 characterized by the fact that said polymerization initiator contains a persulfate.

17. Process as in claim 3 characterized by the fact that it contains the supplementary step of addition of between 0.5 and 10

wt.% of said added monomers of any of the following materials to said dispersion: plasticizers, antifoam agents, pigments, coloring agents and dyes, antibacterial agents, perfumes, pharmaceutical products, enzymes, biologically active agents, agrochemical products, ultraviolet activated agents, stabilizers, rheology modifiers, crosslinking agents and mixtures of these.

18. Process as in claim 3 characterized by the fact that said reaction takes place at a temperature between 40 and 80°C.

19. Aqueous dispersion containing between 15 and 50% by weight of solids which can be obtained by a process as defined in any of claims 1 through 19.

20. Aqueous dispersion as in claim 19 having a particle size between 1 and 60 nm, preferably between 5 and 40 nm.

21. Aqueous dispersion as in claims 19 or 20 also consisting of between 0.5 and 10 wt.% of said added monomers of any of the following materials: plasticizers, antifoam agents, pigments, coloring agents and dyes, antibacterial agents, perfumes, pharmaceutical products, enzymes, biologically active agents, agrochemical products, ultraviolet activated agents, stabilizers, rheology modifiers, crosslinking agents and mixtures of these.

22. Use of the aqueous dispersion as in claims 19 or 20 as a wood preservative, polymer and metal coatings, adhesives, chemical products for waterproofing, textile sizes, agrochemical products, pharmaceutical products, chemical products for the petroleum field, inks, paper products, rheology modifiers, cosmetic products, personal care products, ultraviolet light

diffusion agents, solar screens and biomedical and immunoassay applications.

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# EUROPEAN SEARCH REPORT

## Application No.

Patent Office

EP 94 40 1795

DOCUMENTS CONSIDERED TO BE PERTINENT			
Category	Citation of document with indication if necessary of pertinent parts	claims	INT. CL. OF APPLICATION
X	GB-A 2 049 712 (The Goodyear Tire and Rubber Co.) *claim 1; example 1* -----	1-32	C08F2/16 C09D157/00
A	LU-A 73 643 (Lonza S.A.) ----		
			<div style="border-top: 1px solid black; margin-top: 20px;"> <b>Areas searched</b>  C08F </div>
Location of search The Hague		Date of search 10 January 1995	
<b>CATEGORY OF DOCUMENTS CITED</b> T: theory or principle at basis of invention X: especially pertinent alone      E: older patent document only published on or after Y: especially pertinent in combina-      the application date tion with another document of      O: document cited in the application same category      L: document cited for other reasons A: technological background O: unwritten disclosure      S: Member of same patent family, concordant P: interim literature      document		Examiner Cauwenberg, C.	